# Long-range asymptotic behavior of ground-state wave functions, one-matrices, and pair densities

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The asymptotic behavior of an $N$-electron ground-state wave function is analyzed, as one electron wanders far from the system. Implications for the one-matrix and pair density are described. The asymptotic behavior currently discussed in the literature, in which the remaining $(N-1)$ electrons relax to their ground state, is generalized to the case where the $(N-1)$-electron ground state is degenerate. Infinitely long-ranged correlations are reported, in which the selected $(N-1)$-electron ground state depends upon the direction along which one electron wandered off. We correct a standard limit for the one matrix. Numerical and analytic studies of accurate correlated wave functions illustrate and support the standard asymptotic behavior for the nondegenerate case and its generalization derived here. We extract the $(N-1)$-electron density from the correlated $N$-electron wave function. We also discuss the question how large the separation of one electron must be to realize the limiting behavior. © *1996 American Institute of Physics.* [S0021-9606(96)01531-0]

## I. INTRODUCTION AND SUMMARY OF CONCLUSIONS

The accurate calculation of ground-state properties of atoms and molecules is a major goal in quantum chemistry[1,2] and in density functional theory.[3–5] We focus on the asymptotic behavior of the ground-state wave function $\Psi$ as one spatial coordinate becomes large compared to the extent of the system. Early work on the asymptotic behavior of the wave function yielded upper bounds for the electron density and wave function,[6–11] but we derive equalities.

The motion of an electron far from nuclei occurs on a different time scale from the motion of electrons close to nuclei. The electron loses kinetic energy and slows down as it wanders away. The remaining $(N-1)$-electrons have time enough to adjust themselves to the position of the distant electron. Thus with increasing $r_N$, the remaining $(N-1)$-electron system collapses towards its ground state $\Psi^{N-1}$. [In some cases, e.g., when the total spins of the $N$- and $(N-1)$-electron systems differ by more than 1/2 unit of angular momentum, the ground state of the $(N-1)$-electron system may not be "accessible"[12,13] from that of the $N$-electron system via removal of one electron. In these cases, it should be understood that $\Psi^{N-1}$ is the lowest-energy accessible eigenstate of the $(N-1)$-electron system.] The asymptotic separation of the $N$-particle system allows us to write the leading-order term of the ground-state wave function of the $N$-particle system as

$$\lim_{r_N \to \infty} \Psi(x_1,\ldots,x_N) = \sqrt{\rho(x_N)/N}\,\Psi^{N-1}(x_1,\ldots,x_{N-1})\{x_N\},$$

$$(1)$$

where $x_i = (\mathbf{r}_i, \sigma_i)$ denotes the spatial and spin coordinates of the $i$th electrons, $\rho$ is the electron density, and the curly brackets indicate a parametric dependence of the ground state of the $(N-1)$-particle system $\Psi^{N-1}(x_1,\ldots x_{N-1})\{x_N\}$

upon the coordinates of the $N$th particle. If the ground state of the $(N-1)$-particle system is degenerate, an infinitesimal perturbation causes the $(N-1)$-particle system to switch from one degenerate state to another. The wave function of the $(N-1)$-particle system never becomes independent of the direction $\mathbf{r}_N/r_N$ in which the $N$th particle wanders away. Expressions similar to Eq. (1) have already appeared in the literature,[12–14] but these neglect the parametric dependence on $x_N$. The asymptotic correlation between the $N$th particle and the $(N-1)$-particle system is prefigured in the work of Nisteruk[15] and Slamet *et al.*,[16,17] who found an angular dependence of the asymptotic exchange hole in the noninteracting neon and carbon atoms. However, because they used degenerate $2s$ and $2p$ orbitals, they also found an unphysical $sp$ hybridization.

The asymptotic behavior of Eq. (1) as discussed in the present paper leads to unexpected results for density matrices. We focus on those matrices which contribute to the ground-state energy of the $N$-particle system

$$E = -\frac{1}{2} \int d^3r \nabla^2_{\mathbf{r}'} \gamma(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} + \int d^3r\, \rho(\mathbf{r}) v(\mathbf{r})$$

$$+\frac{1}{2} \int d^3r\, d^3r'\, \frac{P(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},$$

$$(2)$$

where $\gamma(\mathbf{r},\mathbf{r}')$ is the spin-averaged one-particle density matrix, and $P(\mathbf{r},\mathbf{r}')$ is the pair density, defined as the probability density for finding an electron at $\mathbf{r}$ and a second electron at $\mathbf{r}'$, so that

$$\int d^3r' \int d^3r P(\mathbf{r},\mathbf{r}') = N(N-1).$$

$$(3)$$

The on-top value $P(\mathbf{r},\mathbf{r})$ is very accurately given by the local spin density approximation,[18,19] while expressions for $P(\mathbf{r},\mathbf{r}+\mathbf{u})$ as $u \to 0$ have guided the construction of trial wave functions which properly account for the electron–electron cusp.[20–24]

Earlier investigations[12,25] of the large $|\mathbf{r}'-\mathbf{r}|$ asymptotic behavior of the pair density have neglected the consequences of degeneracy. The intuitive expectation that $P(\mathbf{r},\mathbf{r}')$ factorizes into a product of $N$-electron ground-state densities

$$\lim_{|\mathbf{r}'-\mathbf{r}|\to\infty} P(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}') \tag{4}$$

[or equivalently that the pair distribution function $g(\mathbf{r},\mathbf{r}')=P(\mathbf{r},\mathbf{r}')/\rho(\mathbf{r})\rho(\mathbf{r}')$ tends to unity,[26] as it does for a homogeneous electron gas] is incorrect for a finite system (see Fig. 2 of Ref. 27). The commonly used limit[28,29]

$$\lim_{|\mathbf{r}'-\mathbf{r}|\to\infty} P(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}')\left[1-\frac{1}{N}\right], \tag{5}$$

[which satisfies the exact normalization condition of Eq. (3)] is also inexact, even when the $(N-1)$-electron ground state is nondegenerate. We show that

$$\lim_{r\to\infty} P(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\rho^{N-1}(\mathbf{r}')\{\hat{\mathbf{r}}\}, \tag{6}$$

where $\rho^{N-1}(\mathbf{r}')\{\hat{\mathbf{r}}\}$ is one of the degenerate ground-state densities of the $(N-1)$-electron system, with the choice depending parametrically upon the direction $\hat{\mathbf{r}}=\mathbf{r}/r$. Thus a complete factorization in the asymptotic limit is not generally possible, contrary to earlier claims.[12,25] The asymptotic behavior of Eq. (6) is illustrated in Fig. 3–5, and the $(N-1)$-electron ground-state density is extracted from $\Psi^N$ via Eq. (6).

We also find a nontrivial degeneracy effect in $\gamma(\mathbf{r},\mathbf{r}')$, which appears in Eq. (2). The validity of the asymptotic expression

$$\lim_{r,r'\to\infty} \gamma(\mathbf{r},\mathbf{r}') = \sqrt{\rho(\mathbf{r})}\sqrt{\rho(\mathbf{r}')}, \tag{7}$$

as currently given in the literature[5,13,30–32] is limited to nondegenerate $(N-1)$-particle systems. (In Ref. 32 it is incorrectly assumed that, because all natural orbitals decay with the same exponent,[33] they all become equal at large $r$.) More generally, from Eq. (1),

$$\lim_{r,r'\to\infty} \gamma(\mathbf{r},\mathbf{r}') = \sqrt{\rho(\mathbf{r})}\sqrt{\rho(\mathbf{r}')}F(\hat{\mathbf{r}},\hat{\mathbf{r}}'), \tag{8}$$

where

$$F(\hat{\mathbf{r}},\hat{\mathbf{r}}') = \lim_{r,r'\to\infty} \int dx_1\cdots dx_{N-1}\, \Psi^{N-1*}(x_1\ldots x_{N-1})\{\mathbf{r},\sigma\}$$
$$\times \Psi^{N-1}(x_1,\ldots x_{N-1})\{\mathbf{r}',\sigma\}, \tag{9}$$

and $\sigma$ denotes the majority spin channel as $r\to\infty$. $F$ reduces to 1 when the unit vectors $\hat{\mathbf{r}}$ and $\hat{\mathbf{r}}'$ are equal (and could also be calculated from the exact Kohn–Sham wave function[19]). This behavior is illustrated by Figs. 1 and 2 within. Despite the angular factor $F$ in Eq. (8) the simple von Weizäcker expression[34] for the kinetic energy remains valid in the tail region of the electron density.
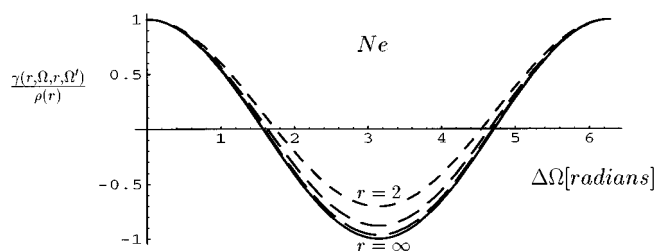


FIG. 1. Angular dependence of the spin-averaged one-particle density matrix $\gamma(r,\Omega,r,\Omega')$ for the Ne atom. The $r$ values of the top to the bottom dashed curves correspond to 2, 3, and 4 $a_0$, respectively. The curves are scaled by the electron density at the corresponding $r$ values. The curve at the very bottom is an exact cosine curve.

Our work has no direct implication for the controversy over the extended Koopmans' theorem,[13,33,35] since that controversy arises even when the $(N-1)$-electron ground state is nondegenerate.[36]

The central object in the exact Kohn–Sham density functional theory[3–5] is the density $\rho_{xc}(\mathbf{r},\mathbf{r}')$ at $\mathbf{r}'$ of the exchange-correlation hole surrounding an electron at $\mathbf{r}$. Levy, Perdew, and Sahni[12] have derived its asymptotic behavior [Eq. (29) of Ref. 12] as the electron moves off to infinity. In light of Eq. (6), their result must be generalized to allow the density of the $(N-1)$-electron system to depend upon the direction $\hat{\mathbf{r}}$ along which the electron is removed. Similar remarks can be made for the exchange hole. Exchange and exchange-correlation holes for atoms are displayed in Ref. 37. The implications of our work for density functional approximations will be discussed elsewhere.[19]

## II. ASYMPTOTIC BEHAVIOR FOR A CLOSED-SHELL ATOM WITH DEGENERATE ($N-1$)-PARTICLE STATES

We illustrate the asymptotic behavior of Eq. (1) using the Ne atom, where the high symmetry ($^1S$ for the atom, $^2P$ for the positive ion) of the system allows a simple derivation. Consider $r_N\to\infty$, and choose the $z$ axis along $\mathbf{r}_N$. Since the $N$-particle wave function has zero total angular
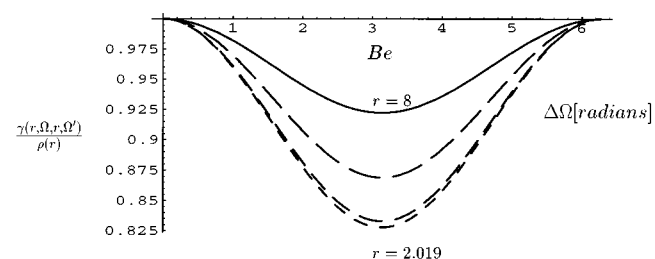


FIG. 2. Angular dependence of the spin-averaged one-particle density matrix $\gamma(r,\Omega,r,\Omega')$ for the Be atom. The $r$ values of the short- to the long-dashed curves correspond to 2.019, 4, 6, and 8 $a_0$, respectively. (The larger the dash, the greater the $r$.) The curves are scaled by the electron density at the corresponding $r$ values.

momentum ($L=0$), the $N$th particle must be in a state with $l=1$ and $m=0$ to have nonzero amplitude along the quantization axis, i.e., along $\mathbf{r}_N$. To conserve total angular momentum, the wave function of the $Ne^+(^2P)$ ion must also have $m=0$. Furthermore, the probability amplitude for finding the $N$th electron at $x_N$ is proportional to $\rho^{1/2}(x_N)$. Therefore,

$$\Psi(x_1,\ldots,x_N) = \sqrt{\rho(x_N)/N} \ \ ^2P_z(x_1,\ldots,x_{N-1})$$
$$= \sqrt{\rho(x_N)/N} \ \ ^2P(x_1,\ldots,x_{N-1})\{x_N\}. \quad (10)$$

The parametric dependence of the $(N-1)$-particle wave function $^2P(x_1,\ldots,x_{N-1})\{x_N\}$ is such that the "hole" in the $Ne^+$ ion is always oriented towards the $N$th electron. This orientation of the $(N-1)$-particle system persists, no matter how large the distance between the $N$th particle and the ion. These considerations apply to all closed-shell atoms, in which the ion is not spherical. More generally, the parametric dependence is not a consequence of the symmetry of the system but of degeneracies of the $(N-1)$-particle ground state.

## III. ASYMPTOTIC BEHAVIOR OF REDUCED DENSITY MATRICES

We define the spin-averaged second-order density matrix by

$$\gamma_2(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1',\mathbf{r}_2') = N(N-1) \int d\sigma_1 \, d\sigma_2 \, dx_3,\ldots,dx_N$$
$$\times \Psi^*(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2,x_3,\ldots,x_N)$$
$$\times \Psi(\mathbf{r}_1',\sigma_1,\mathbf{r}_2',\sigma_2,x_3,\ldots,x_N). \quad (11)$$

The one-particle density matrix is then

$$\gamma(\mathbf{r},\mathbf{r}') = \int d^3\mathbf{r}_2 \ \gamma_2(\mathbf{r},\mathbf{r}_2;\mathbf{r}',\mathbf{r}_2), \quad (12)$$

and the pair density is

$$P(\mathbf{r},\mathbf{r}') = \gamma_2(\mathbf{r},\mathbf{r}';\mathbf{r},\mathbf{r}'). \quad (13)$$

Most of the properties of interest to quantum chemists, e.g., the energy, the charge distribution, or other one-electron properties, can be calculated from these density matrix elements.

Because the asymptotic behavior of the wave function discussed in the literature omits the parametric dependence of the $(N-1)$-particle system on the coordinate of the $N$th electron, it is generally believed that $\gamma(\mathbf{r},\mathbf{r}')$ satisfies Eq. (7).[5,32] We find instead Eqs. (8) and (9). For the Ne atom, the overlap between the $(N-1)$-particle wave functions, which depends on the angle $\Delta\Omega$ between $\mathbf{r}$ and $\mathbf{r}'$ with the Ne nucleus as the apex, behaves like $\cos\Delta\Omega$, because the $Ne^+$ ion has $p$ symmetry. More generally, when the ionization takes place out of a subshell with angular momentum $l$, by inserting Eq. (1) into Eqs. (11) and (12) we obtain

$$\lim_{r\to\infty} \frac{\gamma(r,\Omega,r,\Omega')}{\rho(r)} = \cos(l\cdot\Delta\Omega), \quad (14)$$

which has been verified by calculating the overlap of two spherical harmonics $Y_l^m(\Omega)$ and $Y_l^m(\Omega+\Delta\Omega)$ for $l=1,\ldots,5$. The dependence of $\gamma(\mathbf{r},\mathbf{r}')$ on the angle between $\mathbf{r}$ and $\mathbf{r}'$ gives rise to contributions to both the kinetic and exchange energies.

Neglecting this parametric dependence, Eq. (7) implies

$$\lim_{r\to\infty} -\tfrac{1}{2}\nabla_{\mathbf{r}'}^2 \, \gamma(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} = -\tfrac{1}{2}\rho^{1/2}(\mathbf{r})\nabla^2\rho^{1/2}(\mathbf{r}). \quad (15)$$

After a simple integration by parts, and extending the result for all space, we find the non-interacting kinetic energy to be

$$T_W[\rho] = \frac{1}{8}\int d^3r |\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r}), \quad (16)$$

i.e., the von Weizsäcker approximation.[34] This argument has been used[32] to show that the von Weizsäcker approximation becomes exact in the tail region of the electron density. Our findings show that, for a nonspherical ion, the one-matrix does not factorize, but instead obeys Eq. (8). The asymptotic kinetic energy density then becomes

$$\lim_{r\to\infty} t(\mathbf{r}) = -\tfrac{1}{2}\rho^{1/2}(\mathbf{r})\nabla^2\rho^{1/2}(\mathbf{r}) + \frac{\rho(\mathbf{r})}{2r^2}(L_{\mathbf{r}}^2 F(\hat{\mathbf{r}},\hat{\mathbf{r}}'))_{\mathbf{r}=\mathbf{r}'}, \quad (17)$$

where we have used the identity $\nabla^2 = (1/r) \times (\partial^2/\partial r^2)r - (L^2)/(r^2)$, with $L$ as the angular momentum operator. However, since the second term above is higher order in $1/r$, our results verify that the von Weizsäcker expression yields the right asymptotic kinetic energy density, even when the ion is degenerate.

The asymptotic behavior of the pair density is found by inserting Eq. (1) into Eqs. (11) and (13), yielding Eq. (6), with

$$\rho^{N-1}(\mathbf{r}')\{\hat{\mathbf{r}}_N\} = (N-1)\int dx_2,\ldots,dx_{N-1} \, d\sigma$$
$$\times \Psi^{N-1*}(\mathbf{r}',\sigma,x_2,\ldots,x_{N-1})\{\mathbf{r}_N,\sigma_N\}$$
$$\times \Psi^{N-1}(\mathbf{r}',\sigma,x_2,\ldots,x_{N-1})\{\mathbf{r}_N,\sigma_N\}, \quad (18)$$

where $\sigma_N$ is the majority spin in the limit $r_N\to\infty$. Thus, contrary to expectations,[26] the pair density does not factorize into a product of $N$-particle-system electron densities.

The limit of Eq. (6) obeys the sum rule of Eq. (3) but is not properly symmetric, i.e., $P(\mathbf{r},\mathbf{r}')\neq P(\mathbf{r}',\mathbf{r})$. However, a symmetrized model can be constructed which obeys the same sum rule and has the same limit. This model is

$$P^{\text{model}}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}')n(\mathbf{r},\hat{\mathbf{r}}') + \rho(\mathbf{r})n(\mathbf{r}',\hat{\mathbf{r}})$$
$$- \frac{N}{(N-1)} n(\mathbf{r},\hat{\mathbf{r}}')n(\mathbf{r}',\hat{\mathbf{r}}), \quad (19)$$

where $n(\mathbf{r}',\hat{\mathbf{r}}) = \rho^{N-1}(\mathbf{r}')\{\hat{\mathbf{r}}\}$, and $\lim_{r'\to\infty} n(\mathbf{r}',\hat{\mathbf{r}})/\rho(\mathbf{r}') = 0$.

The results given in this section can be spin decomposed, and Eq. (6) becomes, in an obvious notation,

$$\lim_{r \to \infty} P(\mathbf{r}, \sigma, \mathbf{r}', \sigma') = \rho(\mathbf{r}, \sigma) \rho^{N-1}(\mathbf{r}', \sigma') \{\hat{\mathbf{r}}, \sigma\}. \qquad (20)$$

## IV. NUMERICAL INVESTIGATION OF THE ASYMPTOTIC BEHAVIOR OF GROUND-STATE WAVE FUNCTIONS

We have derived long-range asymptotic expressions for the wave function, the spin-averaged one-particle density matrix, and the pair density. How relevant are these expressions to the problem of constructing electronic wave functions? To address this point, we investigate accurate correlated wave functions for several small systems and compare their asymptotic behaviors with the predictions of the preceding section. The numerical wave functions are obtained from conventional multireference configuration interaction calculations based on Gaussian basis sets. (For details of the calculations, see the Appendix). The wave functions used for Ne and Be recover 88% and 92% of the exact[38] correlation energy, respectively.

In order to understand the asymptotic behavior of $\gamma(\mathbf{r}, \mathbf{r}')$, we choose values of $r = |\mathbf{r}| = |\mathbf{r}'|$ and vary the angle between $\mathbf{r}$ and $\mathbf{r}'$ in the range from 0 to $2\pi$ rad. The corresponding curves for Ne are displayed in Fig. 1. The various $r$ values correspond to 2, 3, and 4 bohr. The angular dependence of the one-particle density matrix for $r = 6 \ a_0$ does not differ from the pure cosine curve on the scale of the above figure. The curves converge towards the cosine curve predicted by Eq. (14) and agree with our expectation about the overlap of two wave functions with $p$ symmetry as a function of the orientation of the $p$ states.

Since the Be ionization takes place out of an $l = 0$ subshell, $\gamma(\mathbf{r}, \mathbf{r}')$ for the Be atom factorizes as $r \to \infty$. However, Fig. 2 shows that this limit is achieved only when $r$ and $r'$ are each extremely large. There is a considerable polarization of the $Be^+$ ion, which in a first approximation can by described by mixing $2p$ character into the $2s$ orbital of the Be atom. This $p$ character then leads to a $\Delta\Omega$ dependence of $\gamma(\mathbf{r}, \mathbf{r}')$ which is noticeable even for rather large $r$. (In the



FIG. 4. Asymptotic collapse of the pair density of the neon atom, plotted along the line joining the outer-electron position to the nucleus. The dashed curves are for $\mathbf{r} = (-3,0,0)$ and $(-5,0,0) \ a_0$. The solid curve is $4\pi r'^2 \rho^{N-1}(\mathbf{r}')\{\hat{\mathbf{r}}\}$.

limit where the nuclear charge $Z$ goes to infinity, the $2s$ and $2p$ orbitals of the four-electron ions become degenerate,[18,39–41] producing a $\Delta\Omega$ dependence even as $r \to \infty$.)

According to the asymptotic equation for the pair density of the ground-state wave function, we can also extract the density of the $(N-1)$-particle system from the pair density of the $N$-particle wave function

$$\rho^{N-1}(\mathbf{r}')\{\hat{\mathbf{r}}\} = \lim_{r \to \infty} \frac{P(\mathbf{r}, \mathbf{r}')}{\rho(\mathbf{r})}. \qquad (21)$$

For any finite but large $r$, $P(\mathbf{r}, \mathbf{r}')/\rho(\mathbf{r})$ gives an approximate $(N-1)$-particle density, and we will refer to this quantity as the ''polarized'' electron density of the $(N-1)$-particle system. Figure 3 shows a plot of $P(\mathbf{r}, \mathbf{r}')/\rho(\mathbf{r})$ for Be. We see that the $1s$ electrons are rather unaffected by the presence of the fixed electron at the distance $r$, whereas the $2s$ electron is quite sensitive to the electron at large separation. As expected, the electron density piles up on the opposite side of the $Be^+$ ion. The deformation of the ion density vanishes very slowly with increasing $r$. The curve labeled $r = \infty$ is just the density of the free positive ion.
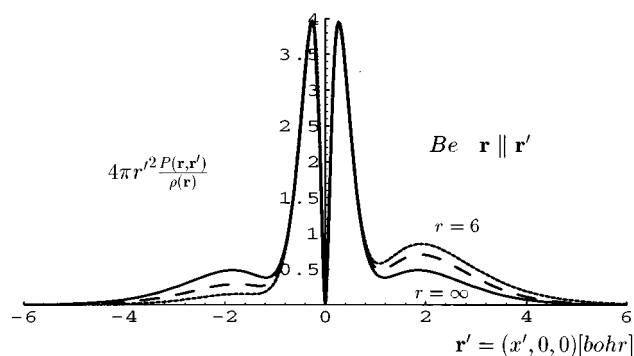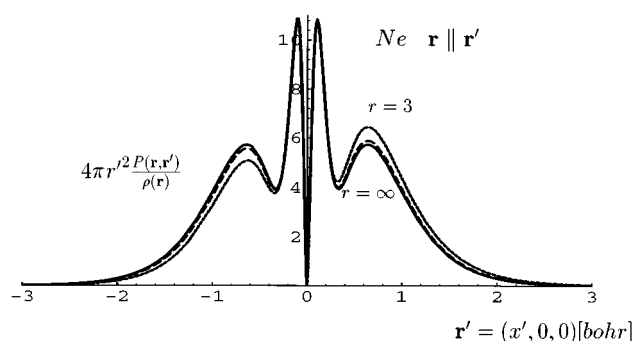


FIG. 3. Asymptotic collapse of the pair density of the Be atom. The dashed curves are for $\mathbf{r} = (-6,0,0)$ and $(-10,0,0) \ a_0$. The solid curve is $4\pi r'^2 \rho^{N-1}(\mathbf{r}')$.
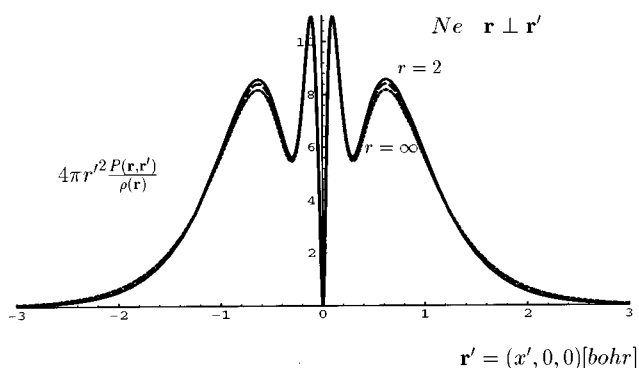


FIG. 5. Asymptotic collapse of the pair density of the neon atom, plotted along a direction through the nucleus and perpendicular to the line joining the outer-electron position to the nucleus. The dashed curves are for $\mathbf{r} = (0, -2,0)$ and $(0, -3,0) \ a_0$. The solid curve is $4\pi r'^2 \rho^{N-1}(\mathbf{r}')\{\hat{\mathbf{r}}\}$.

TABLE I. Gaussian basis sets and resulting energies for Be, Be$^+$, Ne, and Ne$^+$.

| Atom | Basis set | HF energy[a] | MCSCF energy | CI energy | Correlation energy | Exact correlation energy[b] |
|------|-----------|------------|--------------|-----------|--------------------|------------------------------|
| Be | $14s9p4d3f$ | −14.572 99 | −14.618 37 | −14.663 78 | −0.086 43 | −0.094 34 |
| Be$^+$ | $14s9p4d3f$ | −14.277 35 | | −14.321 40 | −0.044 05 | −0.047 37 |
| Ne | $14s9p4d3f$ | −128.546 58 | −128.679 49 | −128.895 94 | −0.349 36 | −0.391 7 |
| Ne$^+$ | $14s9p4d3f$ | −127.819 16 | −127.909 47 | −128.107 16 | −0.288 00 | −0.326 5 |

[a]All energies are given in hartree.
[b]As taken from Ref. 38.

If the orientation of the ion towards the position of the electron at infinite distance is not regarded as a polarization effect, the Ne$^+$ ion is less polarizable than the Be$^+$ ion. We expect that the oriented and polarized Ne$^+$ density converges rapidly towards the density of the oriented free Ne$^+$ ion. This is because the energy gap between the $2p$ orbitals and the $3s$ orbitals is large compared to the $2s-2p$ gap in Be. Figure 4 shows polarized Ne$^+$ densities for $\mathbf{r}$ parallel to $\mathbf{r}'$. Again we find that the $K$-shell electron density hardly changes with $\mathbf{r}$. The calculations for the Ne atom verify that the density of the $(N-1)$-particle system is contained in the pair density of the $N$-particle system, even for approximate wave functions. To illustrate the anisotropy of the pair density at $r=\infty$, we compare the densities in Fig. 4 to polarized densities with $\mathbf{r}$ perpendicular to $\mathbf{r}'$, shown in Fig. 5. The polarization of the density of the $(N-1)$-particle system by the $N$th electron is much weaker in this case. The electron density in the $L$ shell is higher than in Fig. 4, since the hole in the $N$-electron density is oriented along the axis connecting the nucleus to the distant electron.

Finally, we consider Hooke's atom, which consists of two electrons bound to a center by a harmonic potential. For certain values of the spring constant, analytic solutions may be found to this two-body problem.[42] For $k=1/4$, $\Psi(\mathbf{r},\mathbf{r}')$ $= (1+(|\mathbf{r}_1-\mathbf{r}_2|/2)e^{-(r_1^2+r_2^2)/4}/\sqrt{4\pi^{5/2}(8+5\sqrt{\pi})}$. Insertion into Eqs. (12) and (13) and taking $r \gg 1$ yields

$$\gamma(r,\Omega,r,\Omega')/\rho(r) \to 1 + [\cos(\Delta\Omega)-1]/r^2 + \cdots \quad (r \to \infty), \tag{22}$$

and

$$\frac{P(\mathbf{r},\mathbf{r}')}{\rho(\mathbf{r})\rho^{N-1}(\mathbf{r}')} \to 1 - 2\frac{r'}{r}\cos(\Delta\Omega) + \cdots \quad (r \to \infty), \tag{23}$$

where $\Delta\Omega$ is the angle between $\mathbf{r}$ and $\mathbf{r}'$, and $\rho^{N-1}(\mathbf{r}')=e^{-r'^2/2}/(2\pi)^{3/2}$. At $r'=\sqrt{2}$ [the maximum of $4\pi r'^2 \rho^{N-1}(\mathbf{r}')$] and $\mathbf{r}\|\mathbf{r}'$, the polarization correction in Eq. (23) is still significant (10%) at $r=28$.

The examples given in this section demonstrate that the asymptotic behavior discussed prior to this work is incomplete in the case of Ne, and not a very strong constraint on the wave function for either Be or Hooke's atom.

## ACKNOWLEDGMENTS

## APPENDIX: COMPUTATIONAL DETAILS

The calculations reported in the present paper are performed with the COLUMBUS program system,[43,44] which contains a program (UCIDEN) for the construction of the spin-averaged one- and two-particle density matrices[44] of multireference single- and double-excitation CI wave functions. The Gaussian basis sets for all the atoms are taken from the MOLCAS[45] basis set library. The basis sets contained therein are described in Ref. 46. The Gaussians are uncontracted and are transformed to proper spherical components. The COLUMBUS program system has been extended by the program CHARGE to perform the real-space analysis of the spin-averaged one- and two-particle density matrices.

The CI calculations for the Be atom are based on a multiconfigurational self-consistent field (MCSCF) one-particle basis. The MCSCF expansion includes all configurations obtained by distributing two valence electrons in the $2s$, $3s$, and $2p$ orbitals of Be. All configurations obtained by distributing the four electrons of Be in the $1s$, $2s$, $3s$, and $2p$ orbitals in all possible ways are used as references in the CI calculation. Similarly the CI wave function for Be$^+$ was calculated with a set of reference configurations based on the same active orbitals as in the case of Be. The one-particle basis in this case was obtained from a Hartree–Fock (HF) calculation. The wave function for the Ne atom was determined with a multireference single- and double-excited CI calculation, where all zero, single, and double excitations of the eight valence electrons in the $3s$ and $3p$ orbitals are taken as reference configurations. The orbitals were optimized in an MCSCF calculation, where the eight electrons of the $L$ shell have been distributed in all possible ways in two orbitals of $s$ symmetry and six orbitals of $p$ symmetry. The same structure of the MCSCF and the CI wave functions was used in the calculation for Ne$^+$ ion. Table I shows the size of the Gaussian basis sets and the corresponding HF, MCSCF, and CI energies.

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